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MASS SPECTROMETER STUDY OF METAL-CONTAINING FLAMES

FINAL TECHNICAL SUMMARY REPORT

1 September 1961 - 30 November 1967

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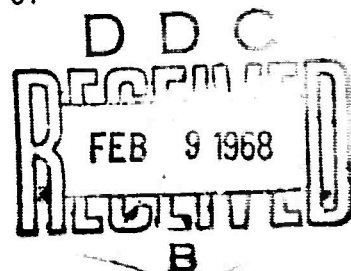
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MASS SPECTROMETER STUDY OF METAL-CONTAINING FLAMES

by

Thomas F. Milne
Frank T. Greene

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1 September 1961 - 30 November 1967

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PREFACE

This report was prepared for the Office of Naval Research under Contract No. Nonr-3599(00), monitored by Mr. Roland Jackel and Dr. Ralph Roberts of the Power Branch, ONR.


The research results obtained during the slightly more than six years' duration of the project "Mass Spectrometer Study of Metal-Containing Flames", are summarized with references to detailed accounts of our work in the open and project literature.

This program has been under the direction of Dr. Thomas A. Milne, Project Leader, and Dr. Frank T. Greene. Dr. Jerome Brewer made valuable contributions during the early phase of the program. Mr. Jacob Beachey has had a major role in the experimental program, while Mr. Gordon Gross and Dr. Sheldon Levy have contributed technical guidance and interest throughout the work. Others who have been involved significantly in various phases are: Dr. Eugene Vandegrift, Dr. William Longley, Mr. Quinton Bowles, Mr. Fred Rollins, Mr. George Vaughn, Mr. Jim Miller, Dr. Lyle Taylor, Dr. Ronald Stearman, Dr. William Glauz, Mr. Douglas Day and Mr. George Vowels.

Valuable consultation and communication with a number of people outside the Institute is acknowledged. These include Professor John Scott, Professor John Fenn, Professor F. S. Sherman, Professor Paul Gilles, Dr. J. K. Cashion, Dr. Robert Fristrom, Dr. Arthur Westenberg, Dr. Arthur Fontijn, Dr. Dan Rosner, and Dr. Dan Golomb. Finally, the efforts of Mr. Thomas Dobbins, Mr. Roland Jackel and Dr. Ralph Roberts in keeping us informed of pertinent work and in introducing our work to others are greatly appreciated.

Approved for:

MIDWEST RESEARCH INSTITUTE


Sheldon L. Levy, Director
Mathematics and Physics Division

30 January 1968

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I. INTRODUCTION

The purpose of this program,^{1/} begun at a time when considerable effort was being expended in characterizing the nature and thermodynamics of gaseous species present in rocket propellant combustion systems, was to employ the burnt-gas region of one-atmosphere, high-temperature flames to provide a self-contained, equilibrated, highly oxidizing environment in which to study gaseous light-metal containing species. The key experimental requirement was to be able to quantitatively sample such species from this environment using cold probes and direct, molecular-beam mass spectrometry.

In 1961, although Kantrowitz and Grey had proposed the use of nozzles as a source of intense molecular beams some ten years earlier, even the empirical requirements for constructing a molecular beam sampling system were not known. Neither was there a good model of the history of the gas during such rapid expansion and of the effects that might accompany such expansions. Consequently our first task, and in fact the major task of this program, was to develop equipment to permit beam formation from one atmosphere, 4000°K flames and equivalent systems; to couple this beam with a mass spectrometer and devise suitable methods of obtaining and interpreting the mass spectral data; and to characterize qualitatively and quantitatively the major phenomena accompanying high-pressure direct sampling which might affect the interpretation of the results. With the techniques and knowledge developed during this program, we applied our high-pressure sampling system to the study of a variety of flame systems, to the determination of the fate of free radicals and condensible species during sampling and to the characterization of the thermodynamics and growth kinetics of weakly bound species.

This final report is intended to give a summary of the research performed, with references to our published work being given should details be desired. Results from the work of numerous people with interests in free-jets and nozzle beams have been invaluable to us in understanding the sampling process. References to this work are given in our publications and reports. Also included in this report, together with our evaluation of the present status of direct sampling, are suggestions of problems in sampling that need further study. We also point out present and future prospects of applying direct sampling techniques and supersonic beams to a variety of practical and scientific problems.

II. DEVELOPMENT OF APPARATUS AND TECHNIQUES FOR SAMPLING HIGH PRESSURE SYSTEMS

The development of the sampling system occurred in three stages. First, and of mainly historical interest, were the attempts to form beams using only mechanical pumping in stage one^{1(3)/*} (pressures of a few hundred microns) and with insufficient attention to orifice-to-second slit (skimmer) spacing or skimmer geometry. Beams from this system were very weak and presumably originated from stagnated gas just in front of the skimmer. Second, with the growth in knowledge of free-jet expansions and the accompanying shock and scattering effects,^{1(4)/} the necessity of keeping stage one pressure low (< 10 microns typically) and orifice-skimmer distances neither too long nor too short, was recognized. Empirical choices of pumps and beam system parameters were made so that quite intense beams could be formed.^{1(6)/} This first, truly direct molecular-beam sampling system used a mechanical shutter for simple analysis of beam versus background intensity.

The third stage of development involved the largely empirical optimization of geometric parameters of the system^{1(8)/} and the incorporation of modulated-beam, phase-sensitive detection techniques^{1(9)/} to measure beam intensities unambiguously. The modulation technique was used also to obtain information about the velocities of neutral beam constituents by a time-of-flight method.^{1(14)/} In fact a new approach to time-of-flight velocity distribution measurements has been conceived,^{1(25)/} employing a unique feature of the Bendix time-of-flight mass spectrometer. The performance of the Bendix mass spectrometer with modulated beams was ascertained under normal and "Studier" continuous operation with an anomalous out-of-phase modulation of background peaks being characterized^{1(15)/} in the latter case. A unique "on-line" comparison of an EAI quadrupole mass spectrometer with the Bendix time-of-flight mass spectrometer was carried out^{1(19)/} over the full mass range of the quadrupole using a modulated beam of argon clusters.

* Quarterly Technical Summary Reports, 1 through 25. 1 Sept. 1961-30 Nov. 1967. "Mass Spectrometer Study of Metal Containing Flames." (Referenced as ^{1(6)/} for the 6th Quarterly, etc.)

A number of inlet systems were developed for the work to be described. For simple beam formation, flat thin orifices as small as 0.0005 in. diameter performed satisfactorily.¹⁽¹⁴⁾ For flame studies water-cooled, spun, conical orifices were used.¹⁽⁵⁾ A few observations of the effect of first-orifice cone angle on beam behavior were made,¹⁽¹⁶⁾ indicating that perturbations may be expected with cone angles less than 90°. For high-pressure, high-temperature isothermal sampling (transpiration experiments) a resistance-heated Ni cell was constructed.¹⁽¹⁸⁾

A variety of flame burners were used ranging from simple torch burners, for C₂N₂-O₂ flames, to flat, screen-type burners for low pressure flame work. The technique of Na line-reversal was used for flame temperature measurements.¹⁽⁶⁾ Beam modulation was accomplished by means of vibrators¹⁽⁹⁾ or motor driven choppers.¹⁽¹⁸⁾

The presently developed sampling system is capable of forming beams from one atmosphere pressure with orifices as large as 0.006 in. diameter. Larger orifices may be used with flames. Much higher pressures can be used if correspondingly smaller orifices are employed. This present system is seriously limited in first stage pumping capability. Stage-one pumping speeds of 10,000 to 30,000 l/sec at 1-10 microns would be desirable. More pumping than is provided by the present second stage 2 in. diffusion pump would also be helpful.

The effective signal/noise capability of the entire system could be considerably improved if a truly bakeable (300-400°C) system was constructed. Modulation could be accomplished with bakeable tuning-fork or vibrating seed choppers. The use of mass spectrometers with continuously operating ion sources might also help in lowering sensitivity limits. The minimum distance achieved between source and detector is 8 in.¹⁽¹⁸⁾ The use of a nude-type mass spectrometer and nested differential pumping ducts could probably reduce this distance to 3-4 in.

III. THE CHARACTERIZATION OF EFFECTS ACCOMPANYING THE HIGH PRESSURE BEAM FORMATION PROCESS

Although the major characterization of free-jet expansions has been done in other laboratories,¹⁹ we found it necessary to investigate, empirically, for our various sampling situations, some of the effects accompanying beam formation and detection. Principal among these were: (1) Mass separation, (2) quenching ability and nucleation, (3) orifice perturbations, and (4) mass spectrometric, electron-impact fragmentation

patterns. These problems will now be briefly reviewed. In addition, although there have been detailed studies of the history of expansion of Ar and N_2 , the expansion behavior of more complex species and mixtures remains to be clarified.

1. The phenomenon of mass separation in the initial continuum expansion, in shocks or other disturbances in the flow, and in the subsequent collimation into a molecular beam had been considered earlier by several groups^{11/} Some measurements of the change in composition had been made, but not under the conditions of interest to our sampling program. Consequently we studied this effect^{1(6)/} with a series of gaseous mixtures, initially at one atmosphere, and established a first-power-of-the-molecular-weight enrichment factor for our high-pressure conditions.^{11/} This is the expected behavior in the absence of shocks and of significant separation in the jet itself. In support of these studies we measured the most probable velocities of components of mixtures such as He-Xe and of argon clusters as large as Ar_{10} in pure argon. We found in every case only negligible lag of the heavier species behind the lighter.^{1(22)/}

We have not systematically studied the effects on mass separation of source pressure, orifice size, angular resolution of the detector, or of chemical nature, molecular weight and composition of mixtures. In many sampling situations of practical interest these parameters may be of great importance. Examples of such situations are the sampling of very large molecules or the sampling of low-pressure flames. The combined use of mass spectrometric detection, precise time-of-flight velocity distribution measurements^{1(25)/} and a versatile high-capacity molecular beam system should allow the straightforward characterization of this phenomenon and provide the data to predict the expected extent of mass separation in any particular application.

2. The problems of the preservation of the true, initial composition of the system being sampled have been studied in two contexts. One of these involved the ability to quench flame reactions, including free radical reactions, which have positive activation energies. The optimum conditions for free-jet formation coincide with the best conditions for such quenching.

A different kind of quenching problem occurs in the case of condensible species and associating systems with zero activation energy. These processes generally have rate constants with negative temperature coefficients so that the approach to quenching must involve a minimum number of collisions during expansion to molecular flow. Again the free-jet expansion appears to best meet this requirement.

The kind of cluster growth observed in other laboratories was verified in our work,^{10,16,18/} a variety of systems were examined and an empirical procedure which involved measurements at a series of orifice sizes was used to detect the presence of nucleation.^{18/} Much more qualitative and quantitative study of the nature and extent of cluster formation in pure gases and mixtures is needed to arrive at even an empirical predictive ability.

3. In the case of high-temperature flames with metal-containing gaseous species, two problems exist. First, the species must survive the expansion to free-molecule flow. The second and much more serious problem occurs when a water-cooled orifice is inserted in these flames. Condensible species deposit rapidly around the orifice tip, causing aerodynamic and thermal perturbation and, ultimately, plugging of the orifice.^{1(22)/}

Orifice interactions were also observed while probing reaction zones of low pressure flames.^{1(16)/} Here one faces a compromise between a highly tapered, conical probe to minimize flame perturbation and a wide-angle cone to optimize free-jet expansion. Some observations were made on the effect of various cone-angles on both of these problems. In the area of the effect of sampling orifice design on beam formation and system perturbation, considerably more work must be done, depending on the particular system being sampled. Such studies should be straightforward.

4. A final major problem which occurs in direct, mass-spectrometric sampling of high pressure systems is that of characterizing the internal energy state of the molecule and determining the effect of that state on the electron impact fragmentation pattern produced by the mass spectrometer. This problem has always been present for the high temperature mass-spectroscopist in the case of molecular-beam sampling of unstable and reactive species for which no fragmentation pattern calibrations can readily be made. The problem becomes particularly acute in high-pressure studies for two reasons. First, one is often dealing with complex molecules and with radicals which are readily confused with fragment ions of other molecules. Further, for complex species, temperature dependent fragmentation is known to be important. Second, the free-jet expansion process produces a presently unknown degree of internal relaxation which introduces a further uncertainty into the mass spectral interpretation. A related problem is the postulated phenomenon of "metastability" in polyatomic clusters.^{16/}

The problems of internal relaxation in free-jets and the effect of temperature and internal state on fragmentation patterns must be studied for a variety of molecules of interest in high temperature sampling situations.

IV. RESULTS OF DIRECT SAMPLING STUDIES

A number of specific research tasks were carried out in addition to the strictly diagnostic studies related to the development of sampling capability. The results obtained are summarized below.

A. Free Radicals in the Burnt-Gas Region of One Atmosphere Flames

In preparation for sampling of metal-containing species in flames, we attempted to quantitatively sample all species present in the (presumably) equilibrated burnt-gas region of one atmosphere H_2-O_2 , $C_2N_2-O_2$ and hydrocarbon- O_2 flames. In general we have been successful in quantitatively sampling such noncondensable species as O, OH, H and Cl from a variety of one atmosphere, hot flames.^{12,15/} Other species such as S, SH, SO, HBO_2 and F could be readily detected,^{15/} and we could observe excess radical concentrations in the reaction zones of one atmosphere flames.^{15/} It seems safe to predict that the extremely rapid cooling achieved in free-jet direct sampling will allow almost any noncondensable species to be quantitatively measured from systems at several atmospheres pressure and temperatures as high as 3000-5000°K.

B. Profiles Through Low-Pressure Flames

Species profiles have been successfully obtained through the reaction zones of 1/20th atmosphere flames.^{24/} The species Br and HBr were successfully followed, for example, through a CH_4-O_2 flame with CH_3Br added. Further, flame-probe interactions were reduced, consistent with good beam formation, to the point where profiles of species such as O_2 , H_2O , CO, CO_2 and CH_4 agreed well with quartz microprobe results. Consequently, a number of immediate applications to flame kinetic problems appear feasible, based on our present knowledge of the sampling process.

C. Sampling Condensible Species From Flames

The major goal of this work, i.e., the determination of the nature and thermodynamic properties of gaseous, light-metal containing species such as $HALO_2$ through the sampling of high temperature flames, was not achieved because of the problem of sampling condensible, nearly saturated species, through cooled orifices. We were never able to positively identify gaseous metal-containing species when Ti, Si, or Fe were added to a variety of hot, one atmosphere flames in concentration levels of 1 percent or less.^{1(22)/} Two reasons which might account for this difficulty are:

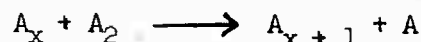
1. The species might simply be condensed during the unavoidable, free-jet expansion part of the sampling process. Studies of the condensation behavior of saturated solutes in one atmosphere transpiration experiments employing isothermal cells and orifices, argue against this explanation.^{9/} It appears that with solute concentrations of 0.1 percent or less, appreciable homogeneous nucleation is unlikely.

2. Such species may fail to survive the sampling process because of interaction with the cooled orifice. In the case of the above metals, oxide layers built up rapidly around and over the typically 0.010 in. diameter orifices at the apex of the water-cooled conical probes used. These layers apparently seriously affected the isentropic expansion through turbulence, boundary layer buildup and heat loss. Although strong beams of noncondensable species such as H_2O , CO_2 , and Cl could be observed when $TiCl_4$ was added to flames, no Ti-containing species^{1(16)/} could be detected. Time-of-flight velocity measurements on noncondensable species in flames, in which added $Fe(CO)_5$ was slowly plugging the orifice, showed progressively lower beam velocities,^{1(22)/} indicative of cooling of the flame gases by the plugging orifice (although the beam intensity was essentially unchanged).

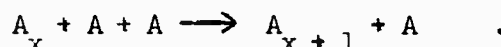
It is obvious that the limitations on the sampling of highly condensable species using cooled probes are severe. Overcoming the plugging problem may require that one deals with large orifices and small concentrations of metal - perhaps 0.1 percent or less in one atmosphere flames unless a mechanical scheme can be devised to permit constant cleaning of the orifice. These changes could cause problems in pumping speed, in signal-noise ratio and in applicability to practical systems. Furthermore, if the orifice size is made too large, homogeneous nucleation effects during free-jet expansion will increase and limit the experiment. Where the orifice can be kept in thermal (if not chemical) equilibrium with the system to be sampled much better results can be expected. The use of orifice-size variation and other techniques to diagnose nucleation effects make it possible that systems with condensable solutes in high concentrations can be managed at high pressure. Thus the coupling of the conventional high-pressure transpiration cell to a mass spectrometer, such as we have done in our isothermal Ni cell studies^{1(18)/} of nucleation of $CsCl$, Hg and other species, appears straightforward.

D. Homogeneous Nucleation in Free Jets

The phenomenon of homogeneous nucleation during the free-jet expansion was studied for its own sake as well as for the purpose of characterizing the problems of sampling. The mass spectrometer observations of the nature and growth of clusters in such expansions^{10/} provides the first direct observation of the earliest, molecular stages of homogeneous nucleation. Of particular interest to us was the growth kinetics of dimers, presumably by three-body recombination. Considerable data were taken for argon and have been reported^{18/} together with the effect of various instrumental parameter on the results. A start has been made toward interpreting dimer growth in pure argon.^{1(24)/} The first attempts to fit rate expressions to the observed Ar_2 data indicate a strongly temperature dependent rate constant with a low efficiency of three-body recombination at 300°K, but with major growth of dimer during the very low temperatures of the final stages of expansion.^{1(25)/} These studies, together with the observation of equilibrium dimer concentrations (of 0.1 percent or more, in many gases), suggest that the growth of higher clusters in the early stages of nucleation may well be through dimers, involved in second order reactions of the form:



rather than the conventionally assumed 3rd order reaction:



The observation of clusters and nucleation behavior in polyatomic species such as N_2 , O_2 , NO and CO_2 ^{16/} suggests that either the dimers of these species are metastable or that they form little parent upon electron impact. Likewise, the effect of solutes on nucleation behavior can be quite pronounced.^{18/} It appears feasible to study the homogeneous nucleation behavior of almost any species, including quite refractory substances such as carbon, under a wide variety of conditions.

The extent of nucleation in nozzle-beam systems in general is in great need of further study in view of the widespread interest and forthcoming use of such beams for a variety of experiments requiring large intensities and high beam energies. The pronounced effects even small amounts of dimer can produce in some kinetic situations are one example of the potential seriousness of nucleation.^{1(21)/}

E. Thermodynamics of Weakly Bound Clusters

The direct sampling of gaseous systems can permit the positive identification and quantitative measurement of equilibrium dimer concentrations. In the case of argon, observed Ar_2 concentrations (in the absence of nucleation effects) are just as predicted by equilibrium calculations based on intermolecular forces ^{18/} An experimental search for equilibrium trimer in argon has been made at cryogenic temperature but without conclusive results ^{1(23)/}

A method of obtaining information about the energy well depth for interaction of such systems has been proposed, based on second-law dimer heat determinations ^{17/}

Although there is currently a problem in interpreting the observed intensities of very weakly bound, van der Waals' dimers of polyatomic gases such as NO , ^{16/} it appears likely that cluster thermodynamics may be determined for more strongly bound systems, such as those involving hydrogen bonds, dipole moments or charge-transfer complexes. We have made preliminary measurements of the free energy of water dimer with major studies in this area continuing for the Office of Saline Water. The application of direct sampling to the determination of energies and structures of hydrogen-bonded systems should be pursued. Even rather large organic molecules of biochemical interest can presumably be studied.

The statistical thermodynamic problem of correctly calculating partition functions and derived thermodynamic quantities, for very weakly bound dimers has been considered. It is very important to correctly consider the very finite number of vibrational and rotational levels present in these molecules ^{1(23)/} Concentrations of "perfectly-stable" polyatomic dimers have been similarly calculated ^{1(22)/}

F. Temperature Dependent Fragmentation Patterns and Internal Energy Relaxation in Free Jets

In the course of our flame studies we obtained evidence of temperature dependent fragmentation of HCl and CO_2 but did not pursue the problem in detail. ^{15/} For a two-fold reason we investigated the temperature dependence of fragmentation of n-butane and, to a lesser extent, of SF_6 using direct high-pressure sampling.

First, the use of modulated beams seemed to offer significant advantages in the determination of fragmentation patterns. ^{27/} The danger of thermal cracking of the gas by the hot filament in the ion source is

eliminated and high gas temperatures can be readily achieved and controlled by the use of heated furnace sources, flames, etc. Furthermore, the application of time-of-flight velocity analyses to different ions can permit detection of the neutral precursors of the ions being measured and can indicate the presence of thermal cracking. Knudsen studies with n-butane over the temperature range of 30°C to 500°C confirmed the previous results of conventional studies with this molecule and indicated negligible reaction at these temperatures.

The second reason for such studies was the need to investigate the effect of pressure, and hence expansive cooling, on the fragmentation pattern of molecules. In a sense, the fragmentation pattern, determined under Knudsen effusion conditions, is used as an internal-energy thermometer to measure relaxational cooling during free-jet expansion. In the case of n-butane the fragmentation pattern varied significantly with pressure at 500°C,¹⁽²⁴⁾ indicating that appreciable relaxation of internal degrees of freedom - almost certainly vibrational - was occurring during expansion. This use of mass spectral patterns as "vibrational thermometers" may provide a simple, reasonably direct measure of vibrational cooling in such expansions.

G. Ionization Properties of Clusters

In the course of nucleation and related studies some observations of cluster ionization behavior were made. Rough appearance potentials for Ar_2^+ ^{18/} and H_3O^+ (presumably from H_4O_2)¹⁽²¹⁾ were made and these indicate the possibility of determining ion-cluster energies. For example, the ions H_3^+ and N_3^+ might be observable from $(\text{H}_2)_2$ and $(\text{N}_2)_2$, respectively, permitting measurements of their binding energy to be made. Extensive fragmentation is possibly present in simple dimers like $(\text{NO})_2$ and $(\text{O}_2)_2$ ^{16/} while the clusters of NH_3 and H_2O apparently ionize principally by loss of NH_2 and OH , respectively.^{10/} The dimer of n-butane appears to give more fragment ions than parent ions, the $58^+/43^+$ ratio being significantly different than for n-butane monomer¹⁽²⁴⁾ and 116^+ being less than either 58^+ or 43^+ . The observation of ions from n-butane clusters up to the tenthmer reveals a series of unusual parent ions of composition $(\text{C}_m\text{H}_{2n+2})_n^+$ or $(\text{C}_y\text{H}_{2y+2n})^+$.¹⁽²⁴⁾

The nature, properties and reactions of such ions deserve further study with free-jet expansions providing a ready source of parent clusters. The measurement of ionization potentials of ever larger clusters provides a gradual transition to the work function of the condensed state.

V. APPLICATION OF DIRECT, HIGH-PRESSURE SAMPLING TO SYSTEMS OF CURRENT INTEREST

Based on our experience to date in direct sampling, we visualize a number of fruitful applications for which the present state of knowledge is sufficient to encourage immediate consideration. These are now briefly discussed.

A. Combustion Systems

Any combustion system which does not produce highly condensible reaction products is a potential candidate for meaningful study by the direct sampling technique which we have been describing. This is not to say that there will not be research problems to be solved in each application, but rather, that on the basis of our work thus far, we are confident that such sampling for reactive and free-radical species can be accomplished. In general, the ability to determine profiles of all major species through combustion zones will aid in determining combustion mechanisms and kinetics. Specifically:

1. The fate and action of inhibitors in flames can be determined. For example, in the case of the halogen-containing inhibitors, one can follow the halogen atom.
2. The combustion reactions leading to the formation and destruction of oxides of nitrogen and sulfur can be measured both in laboratory flames and in actual incinerator systems or internal combustion engines.
3. The burning of gaseous, liquid and solid propellant systems can be studied, as well as simpler systems chosen to give insight into complex real propellants. Examples are H_2-F_2 flames, ammonium perchlorate thermal decomposition and NH_3 -perchloric acid flames.

This section should conclude with the repeated warning that combustion systems which give rise to very refractory reaction products present problems which at the present, to our knowledge, have not been solved.

B. Gas-Surface Reactions

Direct sampling capability should find application in exploring the species and reactions occurring near ablating and evaporating surfaces as well as surfaces chemically reacting with surrounding gases. Examples

of the former would include the decomposition of organic ablators or the evaporation of graphite under heat flux and high pressures. The latter would include such systems as the oxidation of refractory metals at high pressure.

C. Thermochemistry at High Pressure and High Temperature

The coupling of high-pressure, high-temperature isothermal transpiration experiments with molecular-beam sampling opens the way to many interesting thermochemical studies. These could include studies of metal-H₂ systems and refractory metal-halogen systems.

D. Atmospheric Sampling

The direct sampling of species from planetary and earth atmospheres involves the techniques and phenomena we have been discussing. If one desires to sample the reactive species near the surface of Venus, for example, high-pressure direct sampling techniques offer many advantages. Likewise, densities at the entrance orifice of rocket-borne probes in the upper atmosphere may be high enough to involve continuous expansion, shock and mass separation effects.

E. Nucleation Processes

Homogeneous nucleation can be important in a number of situations of practical interest. These include the formation of fallout particles in post-fireball gases, condensation in wind tunnels and rocket nozzles and nucleation of materials released in the upper atmosphere. Another important area is that of nucleation in high-pressure beam systems, where the primary objective is to obtain high energies and large beam fluxes. In all these applications, direct mass spectrometric sampling offers the most direct observation of the processes which occur.

F. Chemical Process Diagnostics and Control

It is readily conceivable that direct, rapid, universal molecular-beam mass spectrometric sampling will find application in industrial chemical processes, both in analyzing the reactions in optimizing design parameters and in rapid-feedback monitoring in automated control systems.

VI. SUMMARY STATEMENTS

A. Present Status of Sampling Knowledge

Sufficient empirical knowledge now exists to permit the design of direct sampling systems capable of achieving reasonably undisturbed gas expansions to molecular flow from pressures up to tens of atmospheres. Temperatures are only limited by the materials problems of the first orifice. Cooled orifices can apparently be used when condensible species are absent. A good approximation to the history of the expansion is provided from current studies of free jets^{19/} The major effects which accompany beam formation are mass separation, nucleation and relaxation of internal degrees of freedom. Broad outlines of these phenomena have been sketched^{19/} The use and advantages of modulated beams and time-of-flight techniques have been explored in terms of signal/noise benefits, interpretation of mass spectral patterns, beam formation diagnostics and source-temperature measurements.^{22/}

B. Further Research Required

Each of the sampling phenomena discussed above needs major quantitative elucidation under the conditions of sampling in particular situations: Mass separation as a function of pressure, orifice size, molecular weight and chemical nature of species and angular resolution of the instrument; nucleation as a function of expansion conditions and bonding and structure of the species involved; and relaxation of internal degrees of freedom in terms of metastability and mass spectrometer fragmentation patterns. Furthermore, the thermal and aerodynamic interaction of the probe with the system needs study in many applied sampling situations, and more work is needed to characterize the effect of probe cone-angle on free-jet expansion and the detailed expansion history to be expected for complex molecules and mixtures.

C. Potential Direct Sampling Applications

Applications which are of immediate, practical interest include the direct study of reactive species in combustion systems such as those involved in the studies of flame inhibition, air pollution, propellant burning and high temperature kinetics. Gas-surface reactions such as ablation and oxidation can be studied at high pressures. The nature and thermodynamics of species important in high temperature systems can be

studied using equilibrium transpiration experiments. The phenomena and techniques for direct sampling of planetary atmospheres can be explored. Nucleation processes such as those which occur in nuclear blasts, in wind tunnels, in rocket exhausts, in chemical releases and in nozzle-beam formation can be studied on a molecular scale. Industrial chemical processes can be studied and controlled through direct sampling.

D. Other Uses for High-Pressure Beams and Sampling

Perhaps as important in the long run as the immediate applications of sampling listed above are the strictly scientific uses of high-pressure beams and sampling techniques. A few of these uses are:

1. The study of the equilibrium and kinetic properties of very weakly bonded clusters including the interaction of molecules at extremely low temperatures.
2. The formation of unusual neutral clusters, such as $(H_2)_2$, from which energies of formation of ions such as H_3^+ can be determined.
3. The determination of the rates of internal relaxation of molecules and the temperature dependence of fragmentation patterns.
4. The application of direct sampling as an analytical tool in a variety of experimental situations involving free radical, condensible and reactive species.
5. The use of the intense beams themselves for molecular beam reaction and spectroscopic studies.

VII. BIBLIOGRAPHY OF REPORTS, PAPERS AND TALKS DEVELOPED
UNDER THE PROGRAM

A. Project Reports (Unpublished) Contract Nonr-3599(00)

1. Quarterly Technical Summary Reports, 1 through 25. 1 Sept. 1961-30 Nov. 1967. "Mass Spectrometer Study of Metal Containing Flames." (References as 1(6) for the 6th Quarterly, etc.)

2. Milne, Thomas A. and Greene, Frank T., "Mass Spectrometric Studies of Reactions in Flames - Quantitative Sampling of Free Radicals From One Atmosphere Flames," 16 July 1965.

3. Milne, Thomas A., "High-Pressure Sampling Conference Report," 23 July 1965.

4. Milne, Thomas A. and Greene, Frank T., "Mass Spectrometric Observations of Argon Clusters in Nozzle Beams. I. General Behavior and Equilibrium Dimer Concentrations," 1 May 1967.

5. Greene, Frank T. and Milne, Thomas A., "Molecular Beam Sampling of Unstable Species From High-Pressure Systems," 1 February 1967.

6. Milne, Thomas A. and Greene, Frank T., "Direct Mass Spectrometric Sampling of High-Pressure Systems," 8 May 1967.

7. Milne, Thomas A. and Greene, Frank T., "A New Method of Obtaining the Well Depth for Weak Intermolecular Potentials," 12 June 1967.

8. Milne, Thomas A. and Greene, Frank T., "The Mass Spectrometric Detection of Dimers of Nitric Oxide and Other Polyatomic Molecules," 24 July 1967.

9. Milne, Thomas A. and Greene, Frank T., "Mass Spectrometric Study of Homogeneous Nucleation in Free Jets," 27 July 1967.

B. Published Papers

10. Greene, F. T. and Milne, T. A., "Mass Spectrometer Detection of Polymers in Supersonic Molecular Beams," J. Chem. Phys., 39, 3150 (1963).

11. Greene, F. T., Brewer, J., and Milne, T. A., "Mass Spectrometric Studies of Reactions in Flames. I. Beam Formation and Mass Dependence in Sampling One Atmosphere Gases," J. Chem. Phys., 40, 1488 (1964).

12. Milne, T. A., and Greene, F. T., "Mass Spectrometric Sampling of One Atmosphere Flames," Tenth Symposium (International) on Combustion, p. 153. The Combustion Institute, 1965.

13. Greene, F. T., and Milne, T. A., "Mass Spectrometric Sampling of High Pressure-High Temperature Sources," "Advances in Mass Spectrometry," Vol. 3, p. 841, The Institute of Petroleum, 1966.

14. Greene, F. T., and Milne, T. A., "Direct High-Pressure Mass Spectrometric Sampling," R/D Magazine, June (1965).

15. Milne, T. A., and Greene, F. T., "Mass Spectrometric Studies of Reactions in Flames. II. Quantitative Sampling of Free Radicals from One Atmosphere Flames," J. Chem. Phys., 44, 2444 (1966).

16. Milne, T. A., and Greene, F. T., "Mass Spectrometric Detection of Dimers of Nitric Oxide and Other Polyatomic Molecules," J. Chem. Phys., 47, 3668 (1967).

17. Milne, T. A., and Greene, F. T., "New Method of Obtaining the Well Depths for Weak Intermolecular Potentials," J. Chem. Phys., 47, 3684 (1967).

18. Milne, T. A., and Greene, F. T., "Mass Spectrometric Observations of Argon Clusters in Nozzle Beams. I. General Behavior and Equilibrium Dimer Concentrations," J. Chem. Phys., 47, 4095 (1967).

19. Milne, T. A., and Greene, F. T., "Direct Mass Spectrometric Sampling of High Pressure Systems," Advances in Chemistry Series, "Applications of Mass Spectrometry in Inorganic Chemistry," Ed. John L. Margrave, ACS Publications, Washington, D. C. (1968).

C. Papers in Preparation

20. Milne, T. A. and Greene, F. T., "Mass Spectrometric Studies of Reactions in Flames. III. Sampling of Condensable Species Using Cold Probes."

21. Milne, T. A. and Greene, F. T., "Mass Spectrometric Observations of Argon Clusters in Nozzle Beams. II. The Growth Kinetics of Dimer."

22. Greene, F. T., Beachey J., and Milne, T. A., "The Use of Modulated Beams with the Bendix Mass Spectrometer."

23. Greene, F. T. and Milne, T. A., "Molecular Beams in High Temperature Chemistry," A review.

24. Milne, T. A., "The Determination of Reaction-Zone Species Profiles Through Direct Mass Spectrometric Sampling."

25. Gosselin, C., Beachey, J., Milne, T.A. and Greene, F. T., "A Direct Comparison of A Quadrupole and Time-of-Flight Mass Spectrometer Using Modulated Beams of Argon Clusters."

26. Milne, T. A. and Greene, F. T., "Partition Functions of Very Weakly Bound Clusters."

27. Beachey, J., Greene, F. T., and Milne, T. A., "Molecular Beam Studies of Temperature Dependent Cracking Patterns and Internal Relaxation in Free-Jets."

28. Milne, T. A. and Greene, F. T., "The Importance of Weakly Bound Dimers in the Early Stages of Homogeneous Nucleation in Rapid Expansions."

D. Technical Presentations of Project Work

a. Gordon Conference on High Temperature Chemistry, New Hampshire, August 1962. Milne.

b. Annual SQUID Meeting, U. of Virginia, Feb. 1963. Milne.

c. JANAF Thermochemical Panel - New York, Nov. 1963. Milne.

d. Annual SQUID Meeting, Cornell, February, 1964. Greene.

e. Tenth Combustion Symposium, Cambridge, August, 1964. Milne.

f. International Mass Spectrometry Meeting, Paris, September, 1964. Greene.

g. Annual SQUID Meeting, Brown University, March, 1965. Milne.

h. High-Pressure Sampling Conference, Kansas City, May, 1965. Greene.

- i. First Midwest High Temperature Chemistry Conference, University of Kansas, June, 1965. Milne.
- j. Annual SQUID Meeting, Rice, March, 1966. Greene.
- k. ASTM-E14, Dallas, May, 1966. Greene.
- l. ACS Meeting, New York, September, 1966. Milne.
- m. Bendix Users Symposium, Cincinnati, October, 1966. Greene.
- n. AIAA Fifth Aerospace Sciences Meeting, New York, January, 1967. Greene.
- o. Annual SQUID Meeting, Purdue, March 1967. Milne.
- p. ASTM-E14, Denver, May, 1967. Milne.
- q. Second Midwest High Temperature Chemistry Conference, Oklahoma State, June, 1967. Greene.
- r. Symposium on Nucleation Phenomena in Gas Dynamics, Annapolis, December, 1967. Milne.

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13. ABSTRACT The results of slightly over six years of research on the direct, mass spectrometric sampling of one atmosphere flames and related high pressure systems are summarized. The empirical development of the sampling system and related problems in detection and data interpretation are outlined. The major phenomena accompanying direct, molecular-beam sampling were found to be: (1) orifice-system interaction, (2) mass separation, (3) nucleation, and (4) influence of internal energy state on fragmentation pattern. Each of these problems has been explored qualitatively and quantitatively. A number of areas of immediate application of direct sampling to practical and scientific problems are listed together with suggestions for future research.			

14. KEY WORDS	LINK A		LINK B		LINK C	
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Direct Sampling						
Nucleation						
Molecular Beams						
Kinetics						
Thermochemistry						
Flames - Combustion						
Clustered Ions						
High Temperature						
Intermolecular Forces						
Modulated Beams						
Fragmentation Patterns						
Free Jets						